

Relativistic coupled-cluster studies of ionization potentials, lifetimes and polarizabilities in singly ionized calcium

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Using the relativistic coupled-cluster method, we have calculated ionization potentials, E1 matrix elements and dipole polarizabilities of many low-lying states of Ca^+ . Contributions from the Breit interaction are given explicitly for these properties. Polarizabilities of the ground and the first excited d-states are determined by evaluating the wave functions that are perturbed to first order by the electric dipole operator and the black-body radiation shifts are estimated from these results. We also report the results of branching ratios and lifetimes of the first excited p-states using both the calculated and experimental wavelengths and compare them with their measured values.

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I. INTRODUCTION

Singly ionized calcium (Ca^+) is an interesting candidate in many areas of physics. It is especially important in astrophysics for investigating the radiative properties of stellar objects [1, 2]. Its transition wavelengths and electric dipole amplitudes are required to find out isotopic abundances [3] and the energy transfers in stars [1, 2]. They are also used for obtaining information on emission and absorption lines of the electric dipole transitions between the low-lying states in galaxies, interstellar gas clouds and gas disks surrounding the stars [1, 2, 4, 5]. Ca^+ is also suitable for laboratory physics. Using the techniques of laser cooling and ion trapping, it has been subjected to many precision measurements, optical frequency methodology, quantum processing and accurate fine structure constant measurements [6, 7, 8, 9, 10, 11, 12]. In these measurements, the knowledge of polarizabilities is necessary to estimate the black-body shift (BBS) and the Stark shift due to the external electromagnetic fields. In our recent works, we have reported the hyperfine structure constants and quadrupole moments in Ca^+ using the relativistic coupled-cluster (RCC) method [13, 14, 15]. The determination of electric dipole polarizabilities requires electric dipole (E1) matrix elements and excitation energies of all the allowed transitions. Due to the importance of these quantities, a number of calculations based on various many-body methods including the sum-over-states approach in the framework of the RCC theory are employed to evaluate them [17, 18, 19, 36]. There

are also measurements of the static dipole polarizability of the ground state in Ca^+ [20, 21], but the results do not agree with each other. In fact, all the calculations [17, 18, 19, 36] differ from the recent measured value [20]. Therefore, it is necessary to carry out thorough investigations of the role of electron correlation, higher order relativistic effects and contributions from the two hole-two particle and the neglected one hole- one particle excited states in the calculations of polarizabilities using an all order *ab initio* approach like the RCC theory. We have developed a novel technique to account for the importance of different correlation effects in these properties for closed-shell and one-valence atomic systems by directly obtaining the atomic wave functions perturbed to first order by the electric dipole operator in the framework of the RCC theory [22, 23]. This method avoids the sum-over-states approach and thereby includes different types of correlation effects in a rigorous manner. This theory has been employed to determine the ground state polarizabilities in a few alkali atoms and singly ionized alkaline earth ions including Ca^+ to check the validity of the theory [22]. Although, the theory for the tensor polarizabilities has been developed, it has not been applied to excited states. In this work, we calculate the E1 matrix elements and excitation energies and employ the above approach to determine scalar and tensor polarizabilities of the 4S and 3D states of Ca^+ . The role of the Breit interaction had not been studied in the earlier works which we investigate here using this *ab initio* method.

There have been recent measurements on the branching ratios from the $4p\ ^2P_{3/2}$ state and the corresponding transition probabilities in Ca^+ [24] which need to be theoretically investigated. We carry out these studies using our *ab initio* approach and by combining our E1 matrix

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elements with the experimental wavelengths and compare with their corresponding experimental results. We also evaluate the lifetimes of the 4P-states using these results.

The remaining part of the paper is organized as follows: In Sec. II, we present a brief outline of the theory. This is followed in Sec. III by a discussion of the method to evaluate the unperturbed and the first order perturbed atomic wave functions using the RCC method. We then present the results and discuss the effect of correlation on various properties in Sec. IV and in the final section we make some concluding remarks.

II. THEORETICAL APPROACH

The static dipole polarizability of a state $|J_0, M_0\rangle$ is given by

$$\alpha_0 = \alpha_0^1 + \frac{3M_0^2 - J_0(J_0 + 1)}{J_0(2J_0 - 1)}\alpha_0^2 \quad (2.1)$$

where α_0^1 and α_0^2 are the scalar and tensor polarizabilities. From the angular momentum selection rule, it is obvious that α_0^2 will be non-zero only for the states with $J_0 > 1/2$. In an explicit form, the expression for the polarizability in the sum-over-states approach can be written as

$$\alpha_0^i = 2 \sum_{n \neq 0} C_i \frac{|\langle J_0 || D || J_n \rangle|^2}{E_0 - E_n}, \quad (2.2)$$

with

$$C_1 = -\frac{1}{3(2J_0 + 1)},$$

$$C_2 = \left[\frac{10J_0(2J_0 - 1)}{3(J_0 + 1)(2J_0 + 1)(2J_0 + 3)} \right]^2 (-1)^{J_0 - J_n} \begin{Bmatrix} J_0 & 1 & J_n \\ 1 & J_0 & 2 \end{Bmatrix}$$

and the E s are the energies of the atomic states. In a single valence system, α_0^i can be divided into three parts in general as follows:

$$\alpha_0^i = \alpha_0^i(v) + \alpha_0^i(cv) + \alpha_0^i(c), \quad (2.3)$$

where v , cv and c inside the parenthesis represent for valence, core-valence and core correlation contributions, respectively. In the sum-over-states approach, it is customary to evaluate $\alpha_0^i(v)$ by calculating the important valence excited states. However, contributions from $\alpha_0^i(cv)$ and $\alpha_0^i(c)$ are generally taken approximately in such an approach. On the otherhand, it is possible to calculate α_0^i exactly in a particular configuration space by evaluating the wave function that is perturbed by the electric dipole operator operator D in the following manner:

Let us rewrite Eq. (2.2) as

$$\alpha_0^i = 2 \sum_{n \neq 0} C_i (-1)^{J_0 - J_n} \frac{\langle J_0 || D || J_n \rangle \langle J_n || D || J_0 \rangle}{E_0 - E_n} \quad (2.4)$$

which in Dirac notation can be expressed as

$$\begin{aligned} \alpha_0^i &= 2 \sum_{n \neq 0} C_i (-1)^{J_0 - J_n} \frac{\langle \Psi^{(0)}(J_0, \gamma) || D || \Psi^{(0)}(J_n, \gamma') \rangle \langle \Psi^{(0)}(J_n, \gamma') || D || \Psi^{(0)}(J_0, \gamma) \rangle}{E_0 - E_n} \\ &= \langle \Psi^{(0)}(J_0, \gamma) || \tilde{D}_i || \Psi^{(1)}(J_0, \gamma') \rangle + \langle \Psi^{(1)}(J_0, \gamma') || \tilde{D}_i || \Psi^{(0)}(J_0, \gamma) \rangle \end{aligned} \quad (2.5)$$

where γ represents parity eigenvalue of the state $|J_0, M_0\rangle$ and γ' is its opposite eigenvalue and we define an effective dipole operator as $\tilde{D}_i = C_i (-1)^{J_0 - J_n} D$. Here, $|\Psi^{(1)}(J_0, \gamma')\rangle$ is the first order perturbation correction to the wave function $|\Psi^{(0)}(J_0, \gamma)\rangle$ due to the dipole operator D and given by

$$|\Psi^{(1)}(J_0, \gamma')\rangle = \sum_{n \neq 0} |\Psi^{(0)}(J_n, \gamma')\rangle \frac{\langle \Psi^{(0)}(J_n, \gamma') || D || \Psi^{(0)}(J_0, \gamma) \rangle}{E_0 - E_n} \quad (2.6)$$

It can be equivalently written as

$$\begin{aligned} |\Psi^{(1)}(J_0, \gamma')\rangle &= \frac{1}{E_0 - H} \sum_{n \neq 0} |\Psi^{(0)}(J_n, \gamma')\rangle \langle \Psi^{(0)}(J_n, \gamma') || D || \Psi^{(0)}(J_0, \gamma) \rangle \\ &= \frac{1}{E_0 - H} \sum_{n, \varrho = \gamma, \gamma'} |\Psi^{(0)}(J_n, \varrho)\rangle \langle \Psi^{(0)}(J_n, \varrho) || D || \Psi^{(0)}(J_0, \gamma) \rangle, \end{aligned} \quad (2.7)$$

since the matrix elements between the same parity states vanish. Applying the completeness condition, we get

$$(H - E_0)|\Psi^{(1)}(J_0, \gamma')\rangle = -D|\Psi^{(0)}(J_n, \gamma)\rangle; \quad (2.8)$$

the above equation can be considered as a first order perturbation equation arising from D . By solving the above equation and Eq. (2.5) it is possible to evaluate α_0^i in the framework of the relativistic coupled-cluster theory.

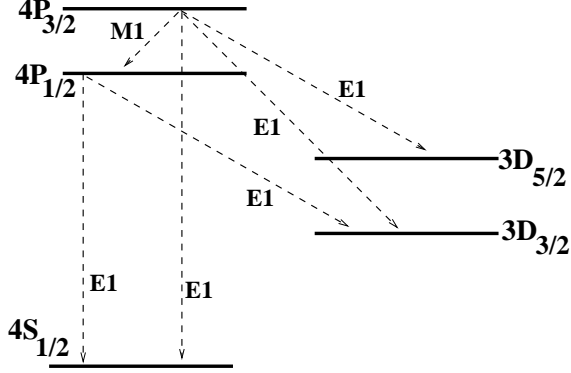


FIG. 1: Schematic low-lying energy level diagrams and decay channels of the P-states in Ca^+ .

The branching ratio (BR) of a state (f) to a lower energy state (i) is defined as

$$\Gamma_{f \rightarrow i} = \frac{A_{f \rightarrow i}}{\sum_i A_{f \rightarrow i}}, \quad (2.9)$$

where $A_{f \rightarrow i}$ is the transition probability of the corresponding transition and sum over i represents total probabilities of all possible transitions. As shown the low-lying energy levels of Ca^+ in Fig. 1, the electrons from the $4p \ ^2P_{1/2}$ state will jump either to the $4s \ ^2S_{1/2}$ or $3d \ ^2D_{3/2}$ states due to the allowed transition with different probabilities. Again, electrons from the $4p \ ^2P_{3/2}$ state will jump to the $4s \ ^2S_{1/2}$, $3d \ ^2D_{3/2}$ and $3d \ ^2D_{5/2}$ states due to the allowed transitions and $4p \ ^2P_{1/2}$ state due to the M1 forbidden transition. The lifetime of the state can be determined from

$$\tau_f = \frac{1}{\sum_i A_{f \rightarrow i}}. \quad (2.10)$$

By combining Eq. (2.9) and Eq. (2.10), it yields

$$A_{f \rightarrow i} = \tau_f \Gamma_{f \rightarrow i}. \quad (2.11)$$

From the same or different measurements of τ_f and $\Gamma_{f \rightarrow i}$, it is possible to estimate the corresponding $A_{f \rightarrow i}$ for various transitions.

The probabilities due to E1 and M1 transitions are given by

$$A_{f \rightarrow i}^{E1} = \frac{2.02613 \times 10^{18}}{(2J_f + 1)\lambda_{f \rightarrow i}^3} |\langle J_f || D || J_i \rangle|^2, \quad (2.12)$$

and

$$A_{f \rightarrow i}^{M1} = \frac{2.69735 \times 10^{13}}{(2J_f + 1)\lambda_{f \rightarrow i}^3} |\langle J_f || M1 || J_i \rangle|^2, \quad (2.13)$$

respectively. In the above equations, $\lambda_{f \rightarrow i}$ is the wavelength of the corresponding transition and it is the reciprocal of the excitation energy (EE).

III. METHOD OF CALCULATIONS

The RCC method which is equivalent to all order perturbation theory has been recently used to obtain precise results and account for the correlation effects in single valence systems [13, 14, 15]. Atomic wave functions for single valence systems can be expressed in the framework of RCC theory as

$$|\Psi_v^{(0)}\rangle = e^T \{1 + S_v\} |\Phi_v\rangle, \quad (3.1)$$

where $|\Phi_v\rangle$ is the reference state constructed from the Dirac-Fock wave function $|\Phi_0\rangle$ of the closed-shell configuration $|1s^2 2s^2 2p^6 3s^2 3p^6\rangle (\equiv |[3p^6]\rangle)$ of Ca^+ by defining $|\Phi_v\rangle = a_v^\dagger |\Phi_0\rangle$ with a_v^\dagger representing addition of a valence electron v . Here T and S_v are the RCC excitation operators which excite electrons from $[3p^6]$ and $a_v^\dagger [3p^6]$ for the corresponding valence electron v , respectively. The amplitudes of these excitation operators are solved by

$$\langle \Phi_v^L | \{ \widehat{H_N e^T} \} | \Phi_0 \rangle = 0 \quad (3.2)$$

$$\begin{aligned} \langle \Phi_v^L | \{ \widehat{H_N e^T} \} S_v | \Phi_v \rangle &= -\langle \Phi_v^L | \{ \widehat{H_N e^T} \} | \Phi_v \rangle \\ &\quad + \langle \Phi_v^L | S_v | \Phi_v \rangle \Delta E_v, \end{aligned} \quad (3.3)$$

with the superscript $L(=1, 2)$ representing the single and double excited states from the corresponding reference states and the wide-hat symbol over $\widehat{H_N e^T}$ represent the linked terms of normal order atomic Hamiltonian H_N and RCC operator T . ΔE_v is the corresponding valence electron affinity (negative of the ionization potential (IP)) energy which is evaluated by

$$\Delta E_v = \langle \Phi_v | \{ \widehat{H_N e^T} \} \{1 + S_v\} | \Phi_v \rangle. \quad (3.4)$$

The EE between two different states are determined from the difference of their ΔE_v s. In Eqs. (3.2) and (3.3) we have considered only the single and double excitations, however we have incorporated contributions from important triple excitations to the ΔE_v calculations. After obtaining the amplitudes for T , the core excitation operator, we solve Eqs. (3.3) and (3.4) simultaneously to

TABLE I: Ionization potentials (in au) of Ca^+ from different works.

State	This work	Others	Expt. [25]
4s $^2S_{1/2}$	-0.43627757	-0.43836 ^a -0.43802 ^b -0.436287 ^c	-0.43627767
3d $^2D_{3/2}$	-0.37396663	-0.37407 ^a -0.37485 ^b -0.373921 ^c	-0.37408278
3d $^2D_{5/2}$	-0.37361011	-0.37379 -0.37448 ^b -0.373921 ^c	-0.37380626
4p $^2P_{1/2}$	-0.32123958	-0.32217 ^a -0.32224 ^b -0.320844 ^c	-0.32149667
4p $^2P_{3/2}$	-0.32025203	-0.32111 ^a -0.32118 ^b -0.320844 ^c	-0.32048108
5s $^2S_{1/2}$	-0.19788645	-0.198293 ^c	-0.19858760
4d $^2D_{3/2}$	-0.17674718	-0.175144 ^c	-0.17729894
4d $^2D_{5/2}$	-0.17665912	-0.175144 ^c	-0.17721142
5p $^2P_{1/2}$	-0.15978307	-0.160060 ^c	-0.16046888
5p $^2P_{3/2}$	-0.15944054	-0.160060 ^c	-0.16011231

^aRelativistic MBPT(2)[26]

^bBrueckner approximation [27]

^cNon-relativistic Coulomb approximation [19].

obtain the amplitudes for the S_v operator. We use the Dirac-Coulomb-Breit Hamiltonian which is given by

$$H = c\vec{\alpha} \cdot \vec{p} + (\beta - 1)c^2 + V_{nuc}(r) + \frac{1}{r_{12}} - \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{r_{12}} + \frac{1}{2} \left\{ \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{r_{12}} - \frac{(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12})}{r_{12}^3} \right\}, \quad (3.5)$$

where c is the velocity of light, α and β are the Dirac matrices and $V_{nuc}(r)$ is the nuclear potential.

We extend the RCC ansatz for the perturbed atomic

state in the presence of the electric dipole operator D as

$$|\tilde{\Psi}_v\rangle = e^{T+\Omega}\{1 + S_v + \Lambda_v\}|\Phi_v\rangle, \quad (3.6)$$

where Ω and Λ_v are the modified RCC operators to the T and S_v operators, respectively. Since Eq. (2.8) is first order in the D operator, the above expression will reduce to

$$|\tilde{\Psi}_v\rangle = e^T\{1 + S_v + \Omega(1 + S_v) + \Lambda_v\}|\Phi_v\rangle. \quad (3.7)$$

Now, separating the above wave function as $|\Psi_v^{(0)}\rangle$ and $|\Psi_v^{(1)}\rangle$, we get

$$|\Psi_v^{(1)}\rangle = e^T\{\Omega(1 + S_v) + \Lambda_v\}|\Phi_v\rangle. \quad (3.8)$$

Following Eq. (2.8), we solve again the amplitudes for the modified operators as

$$\begin{aligned} \langle \Phi^L | \{ \widehat{H_N e^T} \Omega \} | \Phi_0 \rangle &= -\langle \Phi^L | \widehat{D e^T} | \Phi_0 \rangle \\ \langle \Phi_v^L | \{ \widehat{H_N e^T} \} \Lambda_v | \Phi_v \rangle &= -\langle \Phi_v^L | \{ \widehat{H_N e^T} \Omega (1 + S_v) + \widehat{D e^T} (1 + S_v) \} | \Phi_v \rangle + \langle \Phi_v^L | \Lambda_v | \Phi_v \rangle \Delta E_v, \end{aligned} \quad (3.9)$$

where $\widehat{D e^T}$ represent again the connecting terms between D and T operators. In the singles and doubles approximation, we write

$$T = T_1 + T_2 \quad (3.11)$$

$$\Omega = \Omega_1 + \Omega_2 \quad (3.12)$$

$$S_v = S_{1v} + S_{2v} \quad (3.13)$$

and

$$\Lambda_v = \Lambda_{1v} + \Lambda_{2v}, \quad (3.14)$$

where the subscripts $\{1,2\}$ represent the single and double excitations, respectively.

Now the expression for the dipole polarizability follows as

$$\begin{aligned} \alpha_0^i &= \frac{\langle \Psi_v^{(0)} | \tilde{D}_i | \Psi_v^{(1)} \rangle + \langle \Psi_v^{(1)} | \tilde{D}_i | \Psi_v^{(0)} \rangle}{\langle \Psi_v^{(0)} | \Psi_v^{(0)} \rangle} \\ &= \frac{\langle \Phi_v | \{1 + S_v^\dagger\} \overline{\tilde{D}_i} \{ \Omega(1 + S_v) + \Lambda_v \} | \Phi_v \rangle + \langle \Phi_v | \{ \Lambda_v^\dagger + (1 + S_v^\dagger) \Omega^\dagger \} \overline{\tilde{D}_i} \{1 + S_v\} | \Phi_v \rangle}{\langle \Phi_v | \{1 + S_v^\dagger\} \overline{N}_0 \{1 + S_v\} | \Phi_v \rangle}, \end{aligned} \quad (3.15)$$

where we define $\overline{\tilde{D}_i} = (e^{T^\dagger} \tilde{D}_i e^T)$ and $\overline{N}_0 = e^{T^\dagger} e^T$. Generally, both $\overline{\tilde{D}_i}$ and \overline{N}_0 in the RCC approach are each represented by a non-terminating series. However, we

have devised a procedure motivated by physical considerations to deal with them using the Wick's generalized theorem. We evaluate first the effective zero-body, one-body, two body terms etc. systematically and then sand-

TABLE II: Transition matrix elements (in au) from different calculations. Recommended values from our work is given as reco.

Transition	This work			Others
	STOs	GTOs	reco	
4p $^2P_{1/2} \rightarrow 4s \ ^2S_{1/2}$	2.86	2.90	2.88	2.890 ^a 2.866 ^{b,l} 2.861 ^{b,v} 2.898 ^c
4p $^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	2.50	2.41	2.40	2.373 ^a 2.410 ^{b,l} 2.244 ^{b,v}
4p $^2P_{3/2} \rightarrow 4s \ ^2S_{1/2}$	4.02	4.09	4.03	4.088 ^a 4.060 ^{b,l} 4.059 ^{b,v} 4.099 ^c
4p $^2P_{3/2} \rightarrow 4p \ ^2P_{1/2}$	1.15	1.15	1.15	
4p $^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	1.12	1.09	1.09	1.059 ^a 1.076 ^{b,l} 1.028 ^{b,v}
4p $^2P_{3/2} \rightarrow 3d \ ^2D_{5/2}$	3.36	3.28	3.22	3.186 ^a 3.234 ^{b,l} 2.995 ^{b,v} 3.306 ^c

^aRelativistic MBPT(2)[26]

^{b,l}Length gauge result with Brueckner approximation [27]

^{b,v}Velocity gauge result with Brueckner approximation [27]

^cLinearized RCC method [17].

wich them (except zero-body terms) between the S_v , Λ_v and their conjugate operators. We have successfully applied this method in our earlier works [13, 14, 15, 22, 23]. The above zero-body terms, open-terms connecting only with Ω and terms with Λ_v give us core ($\alpha_0^i(c)$), core-valence ($\alpha_0^i(cv)$) and valence ($\alpha_0^i(v)$) correlation effects, respectively.

We also explicitly present contributions from the normalization factors evaluating them in the following way

$$Norm = \left[\langle \Psi_v^{(0)} | \tilde{D}_i | \Psi_v^{(1)} \rangle + \langle \Psi_v^{(1)} | \tilde{D}_i | \Psi_v^{(0)} \rangle \right] \left\{ \frac{1}{1 + N_v} - 1 \right\}, \quad (3.16)$$

where $N_v = \{1 + S_v^\dagger\} \bar{N}_0 \{1 + S_v\}$.

IV. RESULTS AND DISCUSSIONS

We have employed two different types of the basis functions to generate the atomic orbitals; Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). These orbitals are defined on a grid given by

$$r_i = r_0 \left[e^{h(i-1)} - 1 \right], \quad (4.1)$$

where i represents the grid points which we have taken as 750 in total, the step size h is taken as 0.03 in the present case and r_0 is the starting point of the radial distribution from where the electron orbitals become finite and taken as 2×10^{-6} . The STOs and GTOs are given by

$$F^{STO}(r_i) = r^{n_\kappa} e^{-\alpha_i r_i} \quad (4.2)$$

and

$$F^{GTO}(r_i) = r^{n_\kappa} e^{-\alpha_i r_i^2}, \quad (4.3)$$

respectively. Here n_κ is the radial quantum number of the orbitals and α_i is a parameter whose value is chosen to obtain orbitals with proper behavior inside and outside the nucleus of an atomic system. We further define α_i as

$$\alpha_i = \alpha_0 \beta^{i-1}. \quad (4.4)$$

We have considered $\alpha_0 = 0.0975$ and $\beta = 1.77$ for STOs and $\alpha_0 = 0.00525$ and $\beta = 2.83$ for GTOs. However, we have taken 35, 35, 30, 30 and 25 STO and GTO basis functions to construct the s, p, d, f and g orbitals respectively. For RCC calculations, we have considered all the core orbitals and virtual orbitals are considered up to 3500 au for s, p and d symmetries and 1500 au for f and g symmetries in the present calculations. In fact, it is observed that number of virtual orbitals obtained using STOs are more in a given upper energy limit than GTOs while bound orbital energies match well in both the cases. To account for the contributions from the high lying orbitals in some of the properties that we have considered, we have estimated contributions from virtual orbitals using the second order many-body perturbation theory (MBPT(2)) and recommended (reco) results are given by taking into account all these contributions.

In Table I, we present our IP results for the low-lying states and compare them with the corresponding experimental results. These results using STOs and GTOs were consistent. Some IPs from the excited states deviate from the experimental results and it might be possible to improve them by increasing the virtual space. We also compare our results with other theoretical results. Guet and Johnson had employed the relativistic MBPT(2) method to obtain their results [26]. Liaw had employed the Brueckner approximation method to evaluate these energies [27] and his results match with the above MBPT(2) results. In a recent work, Mitroy and Zhang have used a one electron semi-empirical core potential in the non-relativistic framework [19] to estimate these energies which cannot distinguish the fine structure levels. Our method in contrast is *ab initio* and electron correlation effects are included to all orders in perturbation theory in the residual Coulomb and Breit interaction in the one hole-one particle, two hole-two particle and partial three hole-three particle approximation.

We present the E1 and M1 matrix elements in Table II. As can be seen, results from our STOs and GTOs differ for different transitions. We have considered contributions from virtual orbitals from both the basis functions

TABLE III: Transition probabilities (in $\times 10^6 \text{ s}^{-1}$) in Ca^+ .

Transition	This work		Others
	λ^{cal}	λ^{expt}	
$4p \ ^2P_{1/2} \rightarrow 4s \ ^2S_{1/2}$	135.240	134.333	135.26 ^a 132.9 ^b 132.5 ^c 136.0 ^d
$4p \ ^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	9.0431	8.971	8.77 ^a 9.0 ^b 7.8 ^c 9.452 ^d
$4p \ ^2P_{3/2} \rightarrow 4s \ ^2S_{1/2}$	135.842	135.036	138.95 ^a 136.9 ^b 136.9 ^c 139.7 ^d
$4p \ ^2P_{3/2} \rightarrow 4p \ ^2P_{1/2}$	$\sim 10^{-10}$	$\sim 10^{-10}$	
$4p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	1.055	0.962	0.93 ^a 0.95 ^b 0.87 ^c 0.997 ^d
$4p \ ^2P_{3/2} \rightarrow 3d \ ^2D_{5/2}$	8.435	8.419	8.24 ^a 8.5 ^b 7.2 ^c 8.877 ^d

^aRelativistic MBPT(2) is used [26]^bLength gauge result with Brueckner approximation [27]^cVelocity gauge result with Brueckner approximation [27]^dLinearized RCC method is employed [17].

using MBPT(2) and finally given the consistent results as reco values. Guet and Johnson [26] have used B-spline basis based MBPT to obtain these results. Again, Arora *et al.* [17] have also used a B-spline basis but a linearized RCC method to obtain their results. Liaw [27] has used the Brueckner approximation method to get E1 matrix elements in both the length and velocity gauge expressions. Our method intrinsically contains all these many-body effects. We have also evaluated M1 matrix element between the $4p \ ^2P_{3/2} \rightarrow 4p \ ^2P_{1/2}$ transition which is around 1.15 au; almost same with the $3d \ ^2D_{5/2} \rightarrow 3d \ ^2D_{3/2}$ transition [29].

Using the above matrix elements, we determine the transition probabilities and present them in Table III. We have followed two approaches to determine them. First we have considered energies from our calculations and derived wavelengths (λ^{cal}) to obtain the *ab initio* results. In the other case, we use our matrix elements with the experimental wavelengths (λ^{expt}). Although the M1 transition amplitude from the $4p \ ^2P_{3/2}$ state is finite due to a very small fine structure splitting, the corresponding transition probability is almost negligible. We have also compared our results with other *ab initio* and semi-empirical results in the same table. In a recent work,

Gerritsma *et al.* [24] have measured BRs (we discuss these results below in detail) from the $4p \ ^2P_{3/2}$ state and obtain various transition probabilities from this state by combining their results with the lifetime measurements as given by Eq. (2.11). Our results with λ^{expt} match well with their results.

Using the above transition probabilities, we determine BRs from different calculations and present them in Table IV. These results are compared with the recently measured values of the $4p \ ^2P_{3/2}$ state [24]. As presented in this table, our results with λ^{expt} match well the measurements. When we evaluate BRs for the $4p \ ^2P_{1/2}$ and $4p \ ^2P_{3/2}$ states due to 3d states using the relation

$$\Gamma_{f \rightarrow i} = \frac{A_{f \rightarrow i}}{\sum_{i=3d \ ^2D_{3/2}, 3d \ ^2D_{5/2}} A_{f \rightarrow i}}, \quad (4.5)$$

it gives as 14.97 and 14.40, respectively, which are not within the error bar of the existing experimental result [28] and hence require further measurements for verification.

There are a number of experimental lifetime measurements available for the $4p \ ^2P_{1/2}$ and $4p \ ^2P_{3/2}$ states [30, 31, 32, 33, 34, 35] using beam laser, beam foil, beam foil with cascade correction and Hanle techniques. Among them the laser-beam-ion-beam spectroscopy by Jin and Church [30] results are the most precise. Substituting our transition probabilities in Eq. (2.10), we obtain the lifetimes of the $4p \ ^2P_{1/2}$ and $4p \ ^2P_{3/2}$ states as 6.931s and 6.881s with λ^{cal} , respectively, where as 6.979s and 6.924s with λ^{expt} , respectively. Other calculations based on the above discussed results also predict results close to ours. In fact, our result 6.924s of lifetime of the $4p \ ^2P_{3/2}$ state is in good agreement with the experimental results.

Using the same wave functions used to obtain the above properties and solving Eq. (2.8), we obtain the static dipole polarizabilities of the $4s \ ^2S_{1/2}$, $3d \ ^2D_{3/2}$ and $3d \ ^2D_{5/2}$ states with STOs and GTOs and they are presented in Table VI. The dipole polarizabilities for the ground state from STOs and GTOs are in good agreement, but the 3d state dipole polarizabilities differ by 4%. Since we were able to generate less number of virtuals using GTOs in a given energy upper bound, the convergence of these results were checked with virtual orbitals with higher energies which was not possible for STOs due to the computational limitation. Therefore, we consider our results from GTOs are more accurate than results from STOs. There are also a number of theoretical calculations available on both the ground and 3d excited states including our previous work and references therein [17, 19, 20, 22, 36, 37]. We had just carried out the ground state polarizability calculation in Ca^+ along with other atomic systems in the earlier work [22] to verify the validity of the method that was proposed for the first time. In the present case, we have investigated the accuracy of the wave functions in Ca^+ to obtain IPs and E1 matrix elements which are the ingredients to evaluate

TABLE IV: BRs of $4p\ ^2P_{1/2}$ and $4p\ ^2P_{3/2}$ states in Ca^+ .

Transition	This work		Others	Expt [24]
	λ^{cal}	λ^{expt}		
$4p\ ^2P_{1/2} \rightarrow 4s\ ^2S_{1/2}$	0.9373	0.9374	0.9391 ^a 0.9366 ^b 0.9444 ^c 0.9350 ^d	
$4p\ ^2P_{1/2} \rightarrow 3d\ ^2D_{3/2}$	0.0627	0.0626	0.0609 ^a 0.0634 ^b 0.0556 ^c 0.0650 ^d	
$4p\ ^2P_{3/2} \rightarrow 4s\ ^2S_{1/2}$	0.9347	0.9350	0.9381 ^a 0.9354 ^b 0.9443 ^c 0.9340 ^d 0.9357 ^e	0.9347(3)
$4p\ ^2P_{3/2} \rightarrow 4p\ ^2P_{1/2}$	~ 0			
$4p\ ^2P_{3/2} \rightarrow 3d\ ^2D_{3/2}$	0.00726	0.00666	0.00628 ^a 0.00649 ^b 0.00600 ^c 0.00667 ^d	0.00661(4)
$4p\ ^2P_{3/2} \rightarrow 3d\ ^2D_{5/2}$	0.0581	0.0583	0.0556 ^a 0.0581 ^b 0.0497 ^c 0.0593 ^d 0.0643 ^e	0.0587(2)

^aRelativistic MBPT(2) is used [26]^bLength gauge result with MCDF method [27]^cVelocity gauge result with MCDF method [27]^dLinearized RCC method is employed [17]^eSemi empirical [19]

accurate dipole polarizabilities. In fact, the correlation behavior in the 3d state dipole polarizabilities is not discussed in the literature. Patil and Tang [36] had used multipolar-matrix elements based in the non-relativistic approximation to obtain the $4s\ ^2S_{1/2}$ state dipole polarizability. This has got both the summation and integration approach over the intermediate states from different orbital quantum numbers. Using Coulomb approximation with the Hartree-Slater core calculations, Theodosiou *et al.* [20] had reported the dipole polarizability of the same state. Their result differs from ours and it seems as though they have not taken core-correlation into account. Recently, Arora *et al.* [17] and Mitroy and Zhang [19] have also evaluated dipole polarizabilities based on the sum-over E1 matrix elements and oscillator strengths between different states. The main differences in their results and ours is that they have estimated core (neglected for tensor polarizability) and core-valence correlation effects approximately whereas we have used the first order perturbed RCC method to evaluate them. Contributions from the continuum and doubly excited states with configurations like $[4p^5]nsms$ ($n \neq m$, with n, m being prin-

cipal quantum numbers) which are also important for the dipole polarizability calculations of the states have been considered by us. They are implicitly accounted for in the present work by evaluating the first order perturbed wave functions due to the electric dipole operator. We have also corrected our results due to the normalization of the wave functions. In Table VII, we present contributions from the DF and the individual RCC terms obtained using GTOs. The differences between these two results give the correlation contributions associated in evaluating these quantities. It is evident from our studies that correlation effects in the 3d-states are more than 50% while it is about 20% in the $4s\ ^2S_{1/2}$ state. The $\alpha_0^i(c)$ and $\alpha_0^i(cv)$ contributions are found to be smaller for the scalar dipole polarizability than the previously estimated results. We also present these contributions for the tensor polarizabilities which were neglected earlier. Contributions due to the doubly excited states and normalization corrections cannot be neglected in precision calculations. There are three experimental results for the ground state dipole polarizability [20, 21], but they do not match with each other. Although the re-

TABLE V: Lifetimes (in s) of $4p\ ^2P_{1/2}$ and $4p\ ^2P_{3/2}$ states in Ca^+ .

State	This work		Others	Expt
	λ^{cat}	λ^{expt}		
$4p\ ^2P_{1/2}$	6.931	6.978	6.94^a	$7.098(20)^d$
			$7.047^{b,l}$	$7.07(7)^e$
			$7.128^{b,v}$	$7.5(5)^f$
			6.875^c	$6.62(35)^g$
$4p\ ^2P_{3/2}$	6.881	6.924	6.75^a	$6.924(19)^d$
			$6.833^{b,l}$	$6.87(6)^e$
			$6.898^{b,v}$	$7.4(6)^f$
			6.686^c	$6.68(35)^g$
				$6.72(2)^h$
				$6.61(30)^i$

^aRelativistic MBPT(2)[26]

^{b,l}Length gauge result with MCDF method [27]

^{b,v}Velocity gauge result with MCDF method [27]

^cLinearized RCC method [17]. ^dLaser-beam-ion-beam technique[30]

^eLaser-beam techniques [31]

^fBeam foil technique [32]

^gBeam foil technique with cascade correction[33]

^hHanle method [34]

ⁱHanle method [35]

sult given by Theodosiou *et al.* [20] is the latest, but our results are close to Chang [21].

The frequency shift (in Hz) due to a black-body (BBS) due to the frequency-dependent electric field at temperature $T = 300K$ by neglecting the dynamic correction in the $4s\ ^2S_{1/2} \rightarrow 3d\ ^2D_{5/2}$ transition is approximated by [38]

$$\Delta\nu = \frac{1}{2}(831.9\text{V/m})^2 \left(\frac{T(K)}{300}\right)^4 [\alpha_0^1(4s) - \alpha_0^1(3d_{5/2})]4.6$$

By substituting our results in the above expression, we obtain $\Delta\nu = 0.376\text{Hz}$ which is in agreement with $0.38(1)\text{Hz}$ by Arora *et al.* [17] and 0.368Hz by Mitroy

and Zhang [19]. This also supports the measured value $0.39(27)\text{Hz}$ [10]. The agreement between different calculations is mainly due to the cancellation of the results of $4s\ ^2S_{1/2}$ and $3d\ ^2D_{5/2}$ states.

In Table VIII, we present the contributions from the Breit interaction to different properties. These contributions are smaller in these properties than in the hyperfine structure constants which were reported recently [14]. In contrast to the hyperfine constants where the Breit interaction contributes more to the $4s\ ^2S_{1/2}$ state, it is larger in the $3d$ states than the ground state in these properties.

V. CONCLUSION

We have employed the relativistic coupled-cluster method with two different basis functions to study ionization potentials, electric dipole matrix elements and dipole polarizabilities in the singly ionized calcium. We have also evaluated transition probabilities, branching ratios and lifetimes of the first excited p-states using these results. By determining the first order perturbed wave function due to the electric dipole operator, we obtain *ab initio* results for the static dipole polarizabilities in the ground and first excited d-states. Black-body shift in the $4s\ ^2S_{1/2} \rightarrow 3d\ ^2D_{5/2}$ transition has been evaluated using these results and compared with the other available results. Contributions from the Breit interaction to the above properties have been studied for the first time in singly ionized calcium.

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TABLE VI: Polarizabilities (in au) of the $4s\ ^2S_{1/2}$, $3d\ ^2D_{3/2}$ and $3d\ ^2D_{5/2}$ states in Ca^+ .

State	This work				Others		Expt
	GTOs (reco)		STOs		α_0^1	α_0^2	
	α_0^1	α_0^2	α_0^1	α_0^2			
4s $^2S_{1/2}$	73.002		74.342		76.1(1.1) ^a 75.49 ^b 70.872 ^c 70.6 ^d		70.89(15) ^e 75.3(4) ^f 72.5(19) ^g
3d $^2D_{3/2}$	28.504	−15.870	31.604	−17.678	32.73 ^c 25.4 ^d	−25.20 ^c	
3d $^2D_{5/2}$	29.307	−22.492	32.531	−25.516	32.0(1.1) ^a 32.73 ^c 25.4 ^d	−24.5(4) ^a −25.20 ^c	

^aLinearized RCC method is employed [17]^bNon-relativistic sum-over-oscillator strengths approach [19]^cNon-relativistic sum-over-oscillator strengths approach [20]^dNon-relativistic sum-over-oscillator strengths approach [37]^eLifetime measurements and oscillator strengths of [20]^f [21]^g [21].TABLE VII: Contributions from DF and important RCC terms for the dipole polarizabilities. \overline{D}_i and $\overline{D}_i\Omega$ are the core ($\alpha_0^i(c)$) and core-valence ($\alpha_0^i(cv)$) correlation effects, respectively. The remaining terms except *Norm* represent the valence correlation contributions. *Norm* gives the correction due to the normalization of the wave functions.

Terms	4s $^2S_{1/2}$	3d $^2D_{3/2}$		3d $^2D_{5/2}$	
DF	96.201	91.487	-59.261	89.340	-81.330
\overline{D}_i	2.730	2.730	-0.178	2.730	-0.178
$\overline{D}_i\Omega + cc$	0.038	0.151	-0.245	0.268	-0.268
$\overline{D}_i\Lambda_{1v} + cc$	77.283	32.427	-18.317	33.162	-27.573
$\overline{D}_i\Lambda_{2v} + cc$	-1.865	-0.927	-0.271	-0.910	0.618
$S_{1v}\overline{D}_i\Lambda_{1v} + cc$	-2.543	-5.097	2.876	-5.161	4.277
$S_{2v}\overline{D}_i\Lambda_{2v} + cc$	-2.017	-0.298	0.105	-0.289	0.132
Others	0.130	0.161	-0.226	0.161	-0.050
<i>Norm</i>	-0.754	-0.643	0.386	-0.654	0.550

Note: Subscripts $1v$ and $2v$ represent the valence contributions due to the singly and doubly excited states, respectively.

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TABLE VIII: Breit interaction contributions to various properties.

State	Results	
IP (au)		
4s $^2S_{1/2}$	0.00003056	
3d $^2D_{3/2}$	-0.00034491	
3d $^2D_{5/2}$	-0.00027547	
4p $^2P_{1/2}$	0.00005439	
4p $^2P_{3/2}$	0.00002354	
5s $^2S_{1/2}$	0.00001018	
4d $^2D_{3/2}$	0.00003778	
4d $^2D_{5/2}$	0.00001114	
5p $^2P_{1/2}$	0.00001729	
5p $^2P_{3/2}$	0.00000674	
EI elements (au)		
4s $^2P_{1/2} \rightarrow 4s \ ^2S_{1/2}$	0.001	
4s $^2P_{1/2} \rightarrow 3d \ ^2D_{3/2}$	-0.012	
4s $^2P_{3/2} \rightarrow 4s \ ^2S_{1/2}$	0.001	
4s $^2P_{3/2} \rightarrow 3d \ ^2D_{3/2}$	-0.002	
4s $^2P_{3/2} \rightarrow 3d \ ^2D_{5/2}$	-0.005	
Polarizability (au)	α_0^1	α_0^2
4s $^2S_{1/2}$	-0.011	
3d $^2D_{3/2}$	-0.384	0.226
3d $^2D_{5/2}$	-0.499	0.415

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